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LOW-MELTING CRYSTALLIZABLE BOROPHOSPHATE GLASS BINDERS

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Glass ceramic materials that can be used as ceramizing binders for abrasive tools with heat treatment temperatures of 650°C have been developed and tested. Their main physicochemical properties have been investigated.

At present a demand exists in Russia for the development and synthesis of new high-strength glass ceramics on a non-silicate basis, in particular, based on zinc metaborate [1-3]. The majority of known glass binders for electrocorundum abrasive tools have been developed on a silicate basis, which does not always guarantee a strong material. The reason for this is the formation of phases with different CLTEs in the abrasive – glass ceramic transition layer, which leads to disintegration of the material [4]. After a number of experiments it was found that materials based on borophosphate glasses can successfully compete with silicate binders [5].

The purpose of our study was to investigate the possibility of producing low-melting devitrifiable glass binders for producing abrasive tool based on electrocorundum.

The synthesis of glasses was performed in an electric furnace with silit heaters at a temperature of $1000-1200^{\circ}\text{C}$ in glass-carbon crucibles. Samples were molded in graphite molds with subsequent annealing in an electric muffle furnace.

The density of obtained samples was measured by hydrostatic weighing with an accuracy of \pm 0.2 mg and the CLTE was measured using a DKV-4 vertical quartz dilatometer in the temperature interval of $20-600^{\circ}\text{C}$ using the standard method.

The chemical composition of the main crystalline phases was identified by high-precision x-ray phase analysis using a DRON-2 plant with ${\rm Cu}K_{\alpha}$ radiation. The crystallization capacity of the synthesized glasses was studied by the polythermal method by heating samples placed in chamotte boats in a gradient furnace with temperature varying from 500 to 900°C. Differential thermal analysis was performed in quartz crucibles up to a temperature of 1000°C (Paulik – Paulik derivatograph). Bending strength was measured on a tensile-testing machine using the three-point-bending method.

The viscosity of binders was measured using the method of spreading melts over a plane. This method measures not the binding melt viscosity, but its spreadability (fluidity), which is the inverse of viscosity. The spreadability of binders for abrasive tools was measured for the firing temperature of 650°C. It is expressed in percent of the initial sample diameter:

$$R = \frac{D_2}{D_1} \times 100,$$

where D_1 and D_2 are the diameters of the sample before and after spreading, respectively.

Glasses have been synthesized in the system $NaPO_3 - ZnB_2O_3$ adding CaF_2 , LiF, Al_2O_3 , and $Al(PO_3)_3$ (Table 1).

TABLE 1

	Molar content, %			
Glass	NaPO ₃ + Al ₂ O ₃ + Al(PO ₃) ₃ , CaF ₂ , LiF	ZnB_2O_4		
1	30.0	70.0		
2	33.0	67.0		
3	25.0	75.0		
4	33.4	66.6		
5	30.5	69.5		
6	55.0	45.0		
7	52.4	47.6		
8	60.0	40.0		
9	36.4	63.6		
10	39.1	60.9		
11	36.4	63.6		
12	39.1	60.9		
13	39.4	60.6		
14	46.2	53.8		
15	46.2	53.8		
16	50.0	50.0		
17	44.0	56.0		
18	53.8	46.2		
19	57.7	42.3		
20	56.0	44.0		
21	57.3	42.3		

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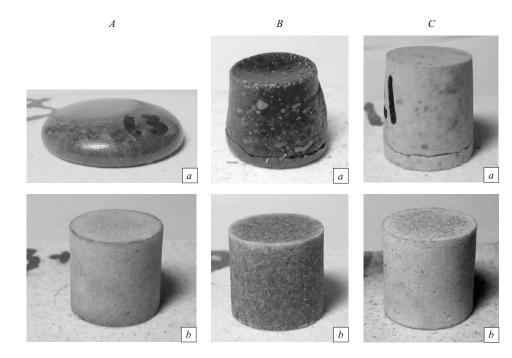


Fig. 1. Glasses 13 (*A*), 19 (*B*), and 21 (*C*) heat-treated at 650°C: *a*) glass; *b*) 30% glass and 70% white electrocorundum 25A F120.

Zinc metaborate ZnB_2O_4 was introduced into the batch via ZnO and H_3BO_3 .

Table 2 gives the results of measuring certain properties of the considered glasses.

The propensity of glasses for crystallization was estimated based on polythermal analysis data. For further investigation we selected glasses with zinc metaborate content equal to 60.6% (glass 13, here and elsewhere molar content)

TABLE 2

Glass	Danaita	Temperature of, °C		OLTE.
	Density, g/cm ³	vitrification	deformation start	CLTE, 10 ⁻⁷ K ⁻¹
1	3.089	475	505	83
2	3.088	468	498	85
3	3.092	483	513	80
4	3.161	498	523	77
5	3.097	503	527	75
6	2.890	402	454	108
7	2.907	406	464	102
8	2.931	354	390	136
9	3.134	485	524	84
10	3.151	470	505	89
11	3.107	480	512	80
12	3.111	465	490	86
13	3.099	493	525	72
14	3.084	452	475	87
15	3.107	448	472	88
16	3.058	445	475	90
17	3.110	417	449	98
18	2.962	430	462	93
19	2.913	402	445	105
20	2.891	387	412	109
21	3.010	417	450	103

and 42.3% (glasses 19 and 21) as the most indicative. Thus, the sample with 60.6% zinc metaborate undergoes no crystallization in the temperature interval of $500-900^{\circ}\text{C}$, whereas crystallization in the samples with 42.3% zinc metaborate proceeded intensely over the whole volume at temperatures close the deformation start temperature. At the same time, the bending strength of glass samples 19 and 21 grew 3-4 times and reached 220-250 MPa. According to the data of x-ray qualitative phase analysis, the products of crystallization are boron orthophosphate BPO₄ and zinc borates ZnB_4O_7 and $\text{Zn}_5\text{B}_4\text{O}_{11}$.

A binder used in the production of electrocorundum abrasive tools has to meet the following requirements: specific surface area over $3000 \text{ cm}^2/\text{g}$, refractoriness not more than 650°C , and spreading on electrocorundum has to be in the interval of 50-130%. Some technical parameters of glasses and their derivatives are given in Table 3. The glass containing 42.3% ZnB₂O₄ has parameters satisfying the above requirements. The shrinkage of samples containing 70% corundum and 30% glass (glass 21) after firing is equal to 3-6%, which permits preserving the geometrical sizes of the products virtually unchanged (Fig. 1). Heating samples

TABLE 3

Glass	Bending strength, MPa, of		Specific	Refracto-	Spreading	Shrinkage of composi-
	glass	crystal- lized sam- ple	surface area, cm ² /g	riness, °C	on electro- corundum, %	tion with 70% corun- dum, %
13	90	_	3190	580	150	6
19	60	250	3234	660	105	3
21	55	220	3462	620	89	3

up to a firing temperature leads to the formation of a glass ceramic material acting as the binding component.

Thus, glass ceramic materials have been obtained that can be used as ceramic binders for abrasive tools (glass 21) with heat treatment temperature of 650°C. The performed studies indicate that the borophosphate glass ceramics considered are promising as binders for abrasive electrocorundum tools.

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